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CERAMIC MATERIALS FOR MILLING BODIES (A REVIEW)

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The parameters of over 40 various types of milling bodies developed or manufactured by domestic and foreign manufacturers are analyzed. It is established that the wear resistance of ceramics depends on two groups of factors: external ones (process characteristics, design specifics of milling machines, shape and size of milling bodies) and internal ones (structure parameters, composition and properties of materials). The structure of ceramics has a deciding effect on the wear resistance of materials of the same type. Wear resistance can be increased by increasing the corundum content in the mixtures or by controlling the microstructure of ceramics by introducing modifying additives. Additives of eutectic compositions are the most promising.

Materials based on aluminum oxide are characterized by a set of important physicochemical parameters, i.e., high strength, hardness, and wear resistance. Such ceramics can be widely used for the production of structural products, including lining elements for mills and milling bodies. The current research in the sphere of wear-resistant ceramics used in milling machines has two directions: improving the properties of uralite and production of totally new types of ceramics.

Uralite is a material containing alumina, clay, and dolomite. The content of aluminum oxide is approximately 75% (here and elsewhere mass content is indicated unless otherwise specified). Milling bodies are made by plastic molding and fired at a temperature usually not exceeding 1420°C [1]. The density of sintered uralite is 2.98 – 3.00 g/cm^3, and the sealed porosity is 1.5 – 2.0%. The bending strength varies within the limits of 120 – 150 MPa, and the size of corundum crystals is 3 – 6 μm. The structure is characterized by the presence of an amorphous isotropic phase, in which mullite crystals of size up to 8 μm are usually found. The content of glass in the material is approximately 20%. When uralite milling bodies are used in industrial conditions, their wear is approximately 0.1 %/h, which contaminates the material milled and leads to frequent repairs of the mill and the need for constant replacement of worn balls with new ones.

The properties of uralite are mainly improved at the expense of increasing the content of oxide aluminum in the mixture introduced in the form of alumina or powder produced by special chemical methods (sol-gel, calcination of salts and aluminum hydroxide, etc.).

Another method for improving the technological properties of uralite balls is the use of special modifying additives, which, first, facilitate the formation of a liquid phase in firing and decrease the sintering temperature and, second, ensure the crystallization of the melt in firing and lead to the formation of a more homogeneous microstructure.

The authors in [2] estimate the possibility of improving the abrasive resistance and hardness of uralite by modifying it with active aluminum oxide and white electrocorundum slime. It is demonstrated that the introduction of Al_2O_3 into the mixture leads to mullite disappearing from the phase composition and to the crystallization of anorthite, whose hardness is higher, which, in turn, ensures increased wear resistance. Unfortunately, the authors do not specify the parameters characterizing the abradability of the material obtained.

The authors of [3] propose a technology for producing milling bodies with increased wear resistance. The firing temperature is 1430 – 1450°C. The optimum composition of mixtures is specified as well: 75 – 80% alumina and up to 15% mineralizers that do not have a colorant effect. The plasticizing additives are refractory clay and bentonite. The modifying additive are talc and dolomite. The developed materials have an average density of 3.31 – 3.34 g/cm^3 and abradability 0.034 – 0.045 %/h.

The authors in [4] propose a ceramic for milling bodies with a decreased sintering temperature (1300 – 1330°C) of the following composition (%): 60 alumina GK, 30 Chasov'-yarskoe clay Ch-1, and 7 dolomite. The additives facilitating the formation of the liquid phase are talcoborate and ZnO. The wear resistance of this material is not inferior to that of uralite.

The authors of [5, 6] have developed ceramics for milling bodies of the following composition (%): 19.0 – 22.0 Veselovskoe clay VGO, 57.0 – 60.0 alumina GK, 8.0 – 9.0 dolomite, 4.0 – 5.0 datolite concentrate, 1.5 – 2.0 rutile, 1.5 – 10.5 manganese ore, 0.0 – 4.0 barium carbonate, and

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0.0 – 3.0 zinc oxide. The material has a decreased sintering temperature (1300 – 1320°C), water absorption of 0.01 – 0.08%, average density 3.25 – 3.27 g/cm^3, and abradability 0.018 – 0.027 %/h. The phase composition of this ceramic includes prismatic corundum crystals of size up to 6 μm, anorthite, and mullite. The presence of a vitreous phase is observed, whose content can reach 40%. [6]. Unfortunately, the paper does not specify the material that was subjected to milling and the milling conditions, which is clearly significant.

The Promkeram JSC has developed milling bodies based on hard porcelain (water absorption not more than 0.5%, average density not less than 2.30 g/cm^3, abradability 0.12 %/h) and high-alumina porcelain (water absorption not more than 0.05%, average density not less than 3.0 g/cm^3, abradability 0.03%/h). The batch of the former material contains (%): 34 – 65 clay, 12 – 40 quartz, and 16 – 30 feldspar, the batch of the latter material includes (%): 60 – 68 clay, 10 – 15 quartz, and 17 – 30 feldspar.

The authors of USSR Inventor's Certif. No. 1648935 proposed a batch for making ceramic wear-resistant articles. To increase its mechanical strength and abrasion resistance, electrocorundum powder with a particle size of 0.1 – 10.0 μm was introduced into the initial mixture. The material contains (%): 65 – 90 ultraporcelain and 10 – 35 corundum.

The SVIT Joint-Stock Company produces milling bodies with aluminum oxide content of 45 – 55%, average density 2.50 – 2.90 g/cm^3, and water absorption not more than 0.05%. The abradability of such materials is 0.036 – 0.100 %/h. Furthermore, the same company produces milling bodies with aluminum oxide content of 80%, average density 3.25 g/cm^3, water absorption not more than 0.05%, and abradability 0.009 %/h.

The Aizovets JSC produces milling bodies with aluminum oxide content 74%, average density 3.20 g/cm^3, and abradability 0.04 %/h. A material with a similar composition and properties was produced by the Eliz JSC.

The Uzhanskoe Vozrozhdenie Production Company has developed ceramics containing 79% aluminum oxide, with average density 3.37 g/cm^3 and abradability 0.035 %/h.

Research in the sphere of materials whose composition resembles that of uralite was carried out abroad in the second half of 1960s. Thus, it is demonstrated in [7] that using alumina of grade corresponding to domestic alumina GK and introducing 30% clay, 7% dolomite, 2% talcoborate, and 1% ZnO makes it possible to produce ceramics of density 3.00 g/cm^3 and abradability 0.1%/h.

According to the data in [8], the milling bodies based on the material with the composition (%): 57.0 – 60.0 alumina, 19.0 – 22.0 clay, 8.0 – 9.0 dolomite, 4.0 – 4.5 datolite concentrate, 1.5 – 2.0 rutile, 1.5 – 10.5 manganese ore, 0.0 – 4.0 barium carbonate, and 0.0 – 3.0 ZnO have average density 3.31 g./cm^3 and abradability 0.022 %/h.

The Kera Company (Holland) has produced a material with 80% Al_2O_3 of average density 3.60 g/cm^3 and abradability 0.1%/h.

The researchers at the D. I. Mendeleev Russian Chemical Engineering University have developed a modified uralite (material Sh-1) with a decreased content of clay and dolomite and with zinc and barium oxides as additives [9]. The quantity of aluminum oxide is around 85%. The temperature of sintering of the material is 1475°C, and its density is 3.55 g/cm^3. This ceramic has abradability 0.027 %/h in model experiments milling electrocorundum and 0.015%/h in experiments on grinding quartz sand.

Another direction in the improvement of wear-resistant ceramics for milling bodies is the development of new materials based on aluminum oxide with a certain quantity of additives, as a rule, lower than that used in the materials of the modified uralite group. The role of such additives consists in decreasing the sintering temperature of ceramics, providing a homogeneous microstructure with a minimum quantity of pores and the vitreous phase, and in the perfect case without a vitreous phase.

Based on RF patent No. 2145312, ceramic materials based on aluminum oxide have been developed, which can be used to produce friction parts operating under abrasive and hydroabrasive wear. This ceramics contains (%): 85.0 – 93.0 Al_2O_3, 3.0 – 5.8 CaO, 2.0 – 4.4 SiO_2, 2.0 – 4.4 B_2O_3, and 0.3 – 0.4 MgO. The sintering temperature of these materials depending on their composition varies in the range of 1330 – 1430°C, and the average density is 3.42 – 3.65 g/cm^3. Unfortunately, data on abradability are not specified, presumably because the main purpose of the innovation was to decrease the sintering temperature of ceramics,.

The Polycor JSC uses corundum milling bodies with mean density 3.70 g/cm^3 and abradability not more than 0.024 %/h. The composition of this ceramics is as follows (%): at least 99.5 Al_2O_3, not more than 0.3 SiO_2, not more than 0.15 Na_2O, and not more than 0.05 Fe_2O_3.

The Kera company (Holland) has developed milling bodies with aluminum oxide content 93.0 – 97.0 %, average density 3.60 – 3.90 g/cm^3, and abradability 0.011 – 0.018 %/h. An increase in aluminum oxide content to 99.5 – 99.9% makes it possible to lower the abradability to 0.0050 – 0.0006 %/h.

The researchers at the D. I. Mendeleev RKhTU have developed wear-resistant materials of two types (Sh-2 and Sh-3) based on aluminum oxide [9]. The ceramic Sh-2 contains 95% Al_2O_3. Its sintering temperature is 1500°C, and its mean density is 3.73 g/cm^3. The abradability of the material is 0.018 %/h in model experiments milling electrocorundum and 0.008 %/h in experiments milling quartz sand.

The material Sh-3 is in fact the ceramic Sh-2 additionally modified by manganese oxide. The temperature of its sintering to a compact state is 1520°C, and its mean density is 3.81 g/cm^3. The abradability of the material Sh-3 is

TABLE 1

No.	Type and grade of material	Mass content of alumina in initial batch, %	Structure			Properties			Published source or manufacturers
			size of corundum crystals, μm	sealed porosity, %	phase compositions (crystals/glass, vol.%)	compression/bending strength, MPa	average density, g/cm^3	water absorption, %	
1	Porcelain	–	4 (mullite)	3.0 – 5.0	40/60	100/–	2.30	0.50	Promkeram JSC, [10]
2	The same	–	4 (mullite)	3.0 – 5.0	40/60	275/–	3.00	0.05	The same
3	Uralite	73.0	3 – 6	1.5 – 2.0	80/20	–/120 – 150	2.99	0.10	Konakovskii Fayans JSC
4	Ts-1, Ts-2	74.0	–	–	85/15	–/240	3.20	–	Éliz JSC
5	Corundum ceramics	98.0	–	5.0	97/3	–/350	3.75	0.00	Éllips-Vit Co., [10]
6	The same	99.6	–	2.0	99.5/0.5	—	3.96	0.00	The same
7	UF-46	79.0	2 – 4	5.0	85/15	1000 – 1500/120 – 180	3.37	0.05	Uzhanskoe Vozrozhdenie Co., [10]
8	AD-20	45.0	–	–	70/30	275/–	2.50	0.05	Svit JSC
9	AD-40	55.0	–	–	80/20	275/–	2.90	0.05	The same
10	AD-65	80.0	–	–	85/15	275/–	3.25	0.05	″
11	Ball	93.5	–	–	90/10	–	3.35	–	Polikor JSC
12	Cylinder	99.5	–	–	100/0	–	3.70	–	The same
13	Ts-1, Ts-2	74.0	–	–	85/15	240/–	3.20	–	Aizovets JSC
14	Corundum ceramics	95.0	4 – 10	3.0 – 4.0	89/11	–	3.50	–	USSR Inventor's Certif. No. 1648935, [10]
15	High-alumina ceramics	75.0	2 – 4	5.0	85/15	340/250	3.34	0.00	[3, 11]
16	The same	80.0	2 – 4	5.0	85/15	300/250	3.31	0.00	[3, 11]
17	″	85.0	2 – 4	5.0	85/15	270/245	3.25	0.00	[3, 11]
18	GB-7M	93.0	–	–	–	–	3.65	0.00	RF patent No. 2145312
19	GB-10M	90.0	–	–	–	–	3.50	0.00	The same
20	GB-15M	85.0	–	–	–	–	3.42	0.00	″
21*, 22**	Sh-1	79.0	5 – 15	2.0 – 3.0	100/0	250/–	3.55	0.00	D. I. Mendeleev RKhTU
23*, 24**	Sh-2	95.0	4 – 10	2.0	100/0	350/–	3.73	0.00	The same
25*, 26**	Sh-3	95.0	4 – 5	0.5	100/0	350/–	3.81	0.00	″
27	High-alumina ceramics	60.0	–	–	–	120 – 150/–	3.00	0.10	[7]
28	The same	57.0 – 60.0	6	–	–	–	3.31	0.05	[8]
29	Keramax	92.0	–	–	–	–	3.60	–	Magotteaux (Belgium)
30	Corundum ceramics	93.0	–	–	85/15	–	3.60	–	Kera (Holland)
31	The same	93.0	–	–	85/15	–	3.60	–	The same
32	″	97.0	–	–	92/8	–	3.70	–	″

0.021%/h in model experiments milling electrocorundum and 0.007 %/h in experiments milling quartz sand.

Table 1 list the properties of main materials used by domestic and foreign manufacturers for milling bodies. In cases where the published sources lacked data on the phase composition of materials, the probable quantity of the vitreous phase was calculated based on the known chemical composition of the batch or found from the petrographic analysis data. The data are summarized in the form of diagrams (Fig. 1).

It should be noted that the data indicted are to a certain extent arbitrary, since many sources did not specify the parameters of testing for wear resistance. Nevertheless, the value of milling obviously depends on many factors, including the kind of material milled, the balls : water : material ratio, the size and the shape of the milling bodies, the volume and the rotational speed of the mill, etc.

However, the available data make it possible (with certain assumptions) to reveal some typical trends. For instance, the improvement of the properties of milling bodies is oriented towards decreasing the share of the vitreous phase in materials and increasing the content of aluminum oxide. No unique relationship between the mean density of ceramics and its abradability was found. This is seen from the data in Fig. 1 and from the results of studying the materials Sh-2 and Sh-3. Despite the fact that the average density of Sh-2 ceramic is significantly lower than that of material Sh-3 (3.73 and 3.81 g/cm^3, respectively), their abradability in model

TABLE 1 (*continued*)

No.	Type and grade of material	Mass content of alumina in initial batch, %	Structure			Properties			Published source or manufacturers
			size of corundum crystals, μm	sealed porosity, %	phase compositions (crystals/glass, vol.%)	compression/bending strength, MPa	average density, g/cm^3	water absorption, %	
33	High-alumina ceramics	80.0	–	–	85/15	–	3.60	–	Kera (Holland)
34	Corundum ceramics	99.5	–	–	98/2	–	3.80	–	The same
35	The same	99.9	–	–	99/1	–	3.90	–	″
36	MZS-3	99.8	2 – 3	–	–	–	3.90	–	Albemarle corporation (Germany)
37	KMS-92	92.0	–	–	–	–	3.70	0.50	The same
38	KMS-94	94.0	–	–	–	–	3.70	0.35	″
39	KMS-96	96.0	–	–	–	–	3.80	0.70	″
40	Alubit 90	90.0	3	–	–	–	3.57	–	Industrie Bitossi SpA (Italy)
41	Eralox	90.0	–	–	–	366/–	3.58	–	Eracles Ceramiche Tecniche (Italy)
42	Corundum ceramics	92.5	–	–	–	340/2200	3.65	–	Ferro Division Ceramica (Italy)
43	P70	70.0	–	–	–	90/483	2.35	–	The same
44	P87	87.0	–	–	–	275/1724	3.50	–	″
45	P90	90.0	–	–	–	335/1462	3.60	–	″
46	P96	96.0	–	–	–	365/1813	3.77	–	″
47	P99	99.0	–	–	–	386/1910	3.94	–	″
48	High-alumina ceramics	60.0	–	–	–	–	–	0.10 – 0.20	[4]
49	The same	57.0 – 60.0	6	–	–	–	3.25 – 3.27	0.01 – 0.08	[5]

* Tested on electrocorundum.

** Tested on quartz sand.

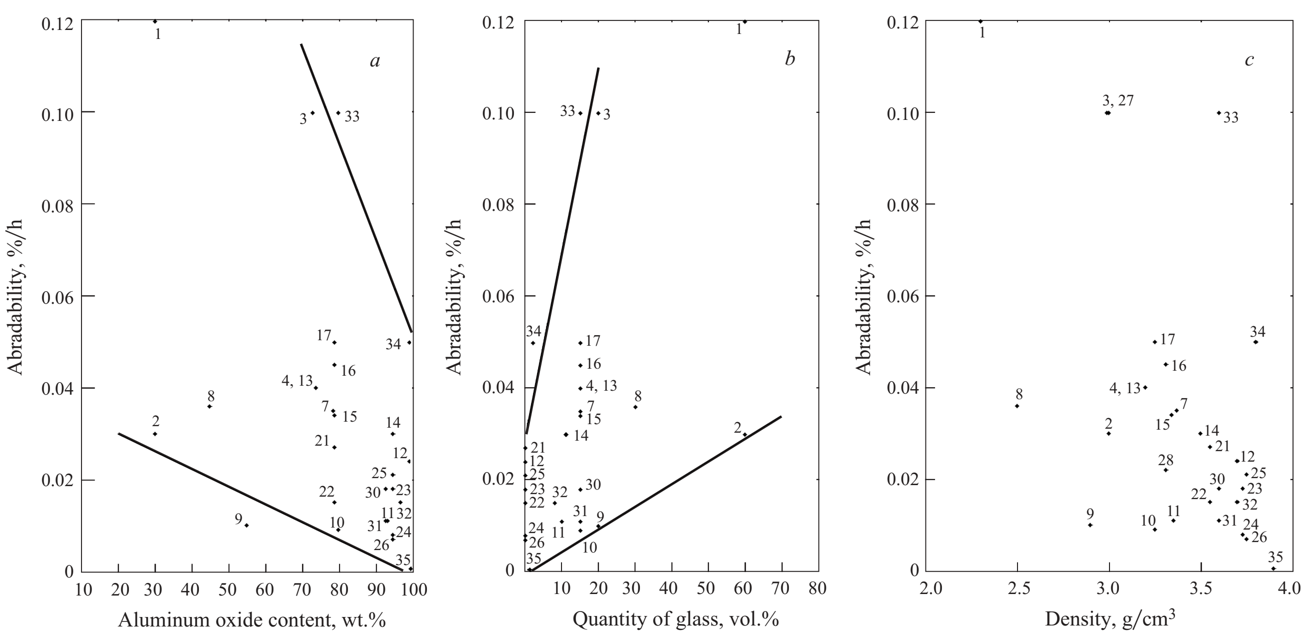

Fig. 1. Abradability – aluminum oxide content in initial batch (*a*), abradability – amount of vitreous phase in ceramics (*b*), and abradability – average density of ceramics (*c*) diagrams for milling bodies of different types. Numbers at the points correspond to the numbers of materials listed in Table 1.

experiments on milling electrocorundum is 0.018 and 0.021 %/h, respectively. Thus, the wear resistance of ceramics will depend on two groups of factors which can be arbitrarily classified into external and internal ones. The external factors include the product characteristics, as well as the design specifics of mills and the shape and size of the milling bodies. The internal factors include the structural parameters and composition and properties of the materials. The structure of ceramics presumably has a deciding effect on wear resistance in the series of a certain type of materials (for instance, high-alumina and corundum).

At first glance the tendency of wear resistance to grow with increasing quantity of Al_2O_3 in the material and with decreasing content of the intermediary boundary phases and the vitreous phase appears obvious. However, the data in Fig. 1 indicate that it is possible to reach a high degree of wear resistance not only by increasing the content of corundum in a mixture but also by regulating the microstructure of ceramics by introducing special modifying additives that crystallize in the course of firing. Additives of eutectic compositions are the most promising in this respect.

REFERENCES

1. V. L. Balkevich, *Engineering Ceramics* [in Russian], Stroiizdat, Moscow (1984).
2. E. G. Ershova, N. I. Protopopova, I. D. Solov'eva, et al., "The phase composition and properties of modified uralite," *Steklo Keram.*, No. 7, 24 (1988).
3. T. G. Kuz'menko, I. V. Kaganova, and A. I. Panashenko, "High-alumina milling bodies," *Steklo Keram.*, No. 2, 23, (1986).
4. A. N. Kuznichenko and I. M. Bogodist, "Ceramics for milling bodies with a decreased sintering temperature," *Steklo Keram.*, No. 8, 20 (1983).
5. N. V. Ishkova, L. S. Opaleichuk, R. S. Krivosheeva, and V. K. Ovchinnikova, "Ceramics for milling bodies with a decreased firing temperature," *Steklo Keram.*, No. 9, 19 (1988).
6. N. V. Ishkova, L. S. Opaleichuk, I. V. Ozerova, and S. P. Bol'shova, "The effect of heat treatment on the phase composition and properties of modified alumina ceramics," *Steklo Keram.*, No. 11, 17 – 19 (1989).
7. *Eur. Conf. on Milling* [Russian translation], Stroiizdat, Moscow (1966).
8. *2nd Eur. Congr. on Milling* [Russian translation], Stroiizdat, Moscow (1968).
9. E. S. Lukin, N. A. Makarov, I. V. Dodonova, et al., "New ceramic materials based on aluminum oxide," *Ogneup. Tekh. Keram.*, No. 7, 2 – 10 (2001).
10. A. M. Batanova and L. S. Bozadzhiev, *Technical Petrography* [in Russian], Izd-vo MGU, Moscow (1987).
11. N. T. Andrianov and E. S. Lukin, *Thermal Aging of Ceramics* [in Russian], Metallurgiya, Moscow (1979).